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(54) Gellan gum fibers.

(57) Gellan gum fibers are produced by extrusion into a gelling salt bath. Optionally, other gums may be co-extruded with the gellan gum. The fibers are useful for the production of wound dressings and catamenial devices.

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BACKGROUND OF THIS INVENTION

Alginate fibers have been known for use in surgical dressings for some time. UK 653,341 is an example of an early disclosure of the use of calcium alginate materials in surgical dressings. The earliest such materials were calcium alginate fibers, but they suffered from the disadvantage of being quite insoluble in water or wound exudate matter. Later a portion of the calcium ions in calcium alginate was exchanged with other cations, whose alginate salts are soluble. UK 653,341 therefore proposed that some of the calcium ions be replaced with sodium ions, to form a mixed salt alginate.

Other uses for alginate fibers have been proposed which involve shaping the fibers as by weaving or knitting into sheets or pads. These materials are useful because they absorb water and swell but retain their shape and structural integrity.

Other polysaccharides have been proposed for fiber formation. For example, Burrow et al. (EP 232,121) have described cross-linked polysaccharides (starch, gellan, curdlan, pullulan, and glycogen) fibers. These cross-linked fibers are produced by extruding a dissolved carboxylate ester of the polysaccharide while simultaneously hydrolyzing the ester groups and cross-linking the resultant hydroxyl groups.

SUMMARY OF THIS INVENTION

It has now been found that gellan gum fibers may be produced by extrusion of a gum solution into a gelling bath. The process, advantageously, does not require esterification and subsequent hydrolysis. The process also produces hybrid fibers comprising gellan and one or more additional gums.

DETAILED DESCRIPTION

By the term "gellan gum", as used herein, is meant the extracellularly produced gum made by the heteropolysaccharide-producing bacterium Pseudomonas elodea, ATCC 31461, by the whole culture fermentation under a variety of conditions of a medium comprising: a fermentable carbohydrate, a nitrogen source, and other appropriate nutrients. Included is the native, deacylated, partially deacylated, and clarified forms therefore. Gellan gum is also known as S-60.

Processes for producing gellan gum are well-known in the art, e.g., U.S. Patents 4,326,052, 4,328,053, 4,377,636, 4,385,126, and 4,503,084.

Particularly preferred is deacylated gellan gum, described in U.S.P. 4,328,052.

In general, gellan gum solutions containing 2-6% gum (percentages herein are on a wt./wt. basis unless stated otherwise) are extruded through fine orifices

5 into coagulating baths containing various cations to produce filamentous fibers which can be used in wound dressings, catamenial devices, etc. Gellan gum may be used by itself or in combination with other polysaccharides such as alginates, xanthan gum, and locust bean gum. Solutions may be extruded cold (room temperature-50°C) or hot (50°-80°C); if hot, the addition of another gum is usually necessary. Gellan gum is especially useful for producing fibers containing magnesium for controlled release of that cation. The fibers may also contain known wound healing agents.

10 When the gellan gum is co-extruded with other polysaccharides, this produces fibers with hybrid properties.

15 The bath of gelling salts is an aqueous solution of 0.5-5% of a soluble salt, the cation of which may be mono-, di-, or tri-valent and selected from those of Groups I, II, and III of the Periodic Table, especially Na⁺, K⁺, Ca⁺⁺, Mg⁺⁺, and Al⁺⁺⁺. Ca⁺⁺ and Mg⁺⁺ are especially preferred. The anion may be chloride sulfate, lactate, phosphate, carbonate, gluconate, or tartrate. Residence time in the bath is 5 seconds - 5 minutes.

20 When a second polysaccharide is used it is one which exhibits a high viscosity when hot; in particular, algin, xanthan gum, and locust bean gum or combinations of these. The second gum can replace up to 33 1/3% of the gellan gum; i.e., up to 2% of a 6% gum solution may be comprised of one or more of a second polysaccharide.

25 In the final product, therefore, the ratio of gellan gum to said second gum is at least 2:1.

30 By algin is meant the soluble derivatives of alginic acid, which may be chemically extracted from all species of Phaeophyceae, brown algae. The term is intended to include the soluble salts of alginic acid (e.g., sodium, potassium, or ammonium alginate) and the salts of its ethers (e.g., propylene glycol alginate).

35 By xanthan gum is meant the biosynthetic polysaccharide produced by the organism Xanthomonas campestris by the whole culture fermentation of a medium comprising a fermentable carbohydrate, a nitrogen source and appropriate other nutrients.

40 Xanthan gum preparation is described in numerous publications and patents, e.g., U.S. Pat. Nos. 3,671,398; 3,594,280; 3,591,578; 3,481,889; 3,433,708; 3,427,226; 3,391,061; 3,391,080; 3,271,287; 3,251,749; and 3,020,206.

45 Locust bean gum (lbg) is an extract of the locust bean or carob, Ceratonia siliqua. It is commercially available and used as a stabilizer in foods such as ice cream, sausages, and cheese.

50 Gellan gum is normally gelled by heating an aqueous solution to dissolve the gum then simply cooling to produce a gel, provided cations are present. It is also known that solutions may be prepared cold in distilled or deionized water by the addition of

a small amount of sequestrant. The sequestrants which can be used in this invention include triodium orthophosphate (TSP), ethylenediaminetetraacetic acid (EDTA), sodium citrate, tetrasodium pyrophosphate (TSPP), sodium hexametaphosphate (Calgon) and the like. Gellan gum fibers can therefore be prepared by forcing a solution of 2.0% deacylated, clarified gellan gum containing 0.25% sodium citrate in deionized water through a nozzle having a diameter of eleven thousandth of an inch into a 2% calcium chloride bath where fiber formation immediately occurs.

Gellan gum is particularly useful for forming fibers containing magnesium ions as it also gels in the presence of magnesium salts. The 2% gellan gum solution above was also forced into a bath containing 2% magnesium sulfate wherein fiber formation also immediately occurred. Fibers containing a source of magnesium are valuable additives to catamenial devices such as tampons where magnesium ions are said to prevent toxic shock syndrome. Magnesium alginate is soluble in water; therefore it cannot be formed by useful methods but must be formed by ion exchange from insoluble calcium alginate fibers already produced by the usual methods. A small amount can be formed simultaneously with gellan gum fibers however, by incorporating sodium alginate into gellan gum solutions before extrusion into the gelling bath. Up to about 25% sodium alginate based on the weight of the gellan gum is possible without destroying the fiber integrity. Thus, 2.0% gellan gum plus 0.5% alginate having a viscosity of 95,000 cP as measured on a Brookfield LVT viscometer, spindle 4, 6 rpm, 25°C was extruded into a bath containing 2% magnesium sulfate wherein gelation and fiber formation immediately occurred. Since the alginate tends to swell slightly the bath may also contain up to 50% of a lower alcohol such as isopropanol to minimize swelling. The same solution above was extruded into a 2% calcium chloride bath where fiber formation immediately occurred.

Fiber formation from hot solutions is more complicated. Gellan gum solutions have high viscosity when cold but low viscosity when heated, which makes it possible to prepare more concentrated solutions which gel more rapidly with higher gel strength. Fiber production by extrusion from hot gum solutions into a bath were not successful, however, because the low viscosity solution dispersed into floes without forming a continuous fiber. It has been found that the addition of another polysaccharide which produces more viscosity at temperatures of 50-80°C make fiber formation possible. Thus, a hot 4% gellan gum solution forced through a nozzle into a 2% calcium chloride bath instantly dispersed while a 4% gellan gum solution containing 1% sodium alginate having a viscosity of 4,400 cP as measured on a Brookfield LVT viscometer, spindle 4, 60 rpm, 70°C formed fibers under

the same conditions. The high viscosity thickeners xanthan gum and locust bean gum or a combination of the two also produced fibers when combined with the gellan gum at levels of 0.5-1.0%.

The fibers of this invention can be used in various forms. If a non-woven fabric is to be prepared, and this is the fabric of choice, a cotton card may be used to form a web, which may then be cross-lapped and then needle punched in conventional equipment.

If a woven fabric is to be prepared, the fibers may be carded and then spun into a yarn, which can be woven in a conventional loom. Alternatively, the fibers may be collected in a spinning box, according to the method of Tallis (UK 568,177) and woven. If a knitted fabric is to be prepared, the fibers can be prepared as a continuous filament yarn (again according to UK 568,177) which is then knitted on a conventional knitting machine.

The fiber end product (e.g., a pad) may include one or more antimicrobial (for example, antibacterial or antifungal) agents and/or one or more local anesthetics (for example, procaine) and additionally or alternatively one or more pharmaceutical agents.

Claims

1. A fiber comprises gellan gum and one or more of a second gum, which is algin, xanthan, or locust bean gum, wherein the ratio gellan gum to said second gum is at least 2:1.
2. A method of producing gellan gum fibers which comprises extruding a 2-6% gellan gum solution into a coagulating bath comprising 0.5-5.0% gelling salts.
3. The method of Claim 2 wherein the gelling salts are of calcium or magnesium.
4. The method of Claim 2 wherein the gum solution comprises one or more of a second gum, which is algin, xanthan, or locust bean gum, and wherein the ratio of gellan to said second gum is at least 2:1.